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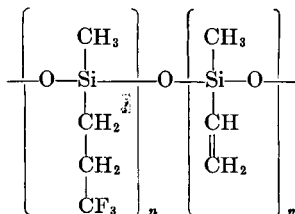# ACCELERATED HEAT-AGING STUDIES ON FLUOROSILICONE RUBBER*

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INTRODUCTION

The nature and extent of chemical changes that take place in a number of selected elastomers at long times has been under study. Previously, an investigation of the chemical degradation of styrene–butadiene rubber (SBR) was reported[1]. Presently, a fluorosilicone gum rubber (FVMQ) and its peroxide vulcanizate are under examination. The general purpose of these investigations is to gather information pertinent to understanding the basic mechanism of aging.

The fluorosilicone elastomer used in this work can be regarded as poly-(γ,γ',γ''-trifluoropropylmethyl)siloxane containing less than 0.5 wt.% vinyl-methylsiloxane as comonomer.

$$\left[\begin{array}{c} CH_3 \\ | \\ -O-Si- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CF_3 \end{array} \right]_n \quad \left[\begin{array}{c} CH_3 \\ | \\ O-Si-O- \\ | \\ CH \\ \| \\ CH_2 \end{array} \right]_m$$

Silicones are noted for their resistance to extremes of temperature, but they lack resistance to hydrocarbon-based fuels and lubricating oils used in aircraft. Fluorine-containing silicones remedy this situation to a large extent. The position of the fluorine atom on the alkyl side chain influences the thermal and hydrolytic stability of the molecule. Less stable compounds are obtained when the fluorine atoms are placed in the α or β positions[2,3] as compared to γ or δ positions. The vinyl groups provide reactive sites for crosslinking (vulcanization).

Several methods were used to determine the network changes that take place when the fluorosilicone elastomer is heat aged. These were (1) infrared spectroscopy, (2) gel permeation chromatography (GPC), (3) thermogravimetric analysis or weight-loss measurements, and (4) stress-relaxation measurements. This article discusses the information obtained from these measurements.

EXPERIMENTAL

PREPARATION OF VULCANIZATES

Two batches of vulcanizates using 0.2 and 0.05 wt.% of dicumyl peroxide (Di-Cup) were prepared from LS 420 fluorosilicone gum (FVMQ, Dow Corning

N77-70831

Corp). This peroxide was selected as the vulcanizing agent because its decomposition products are volatile and leave no residue that might enhance the degradation of the rubber. Sheets 1.52 to 1.78 mm thick were made. Best results were obtained when the rubber was kept 18–20 min in a preheated mold at 93°C under high pressure. Vulcanization was completed by further heating at 160°C for 1 h. From stress–strain measurements carried out on strips of vulcanizates swelled to equilibrium in butyl acetate, the network chain concentrations ν_e were calculated to be 28.8 mol/m^3 for the vulcanizate containing 0.2% of peroxide and 10.0 mol/m^3 for the vulcanizate containing 0.05% peroxide.

INFRARED SPECTROSCOPY

A Perkin-Elmer Model 421 spectrophotometer was used. Films 0.05–0.07 mm thick were cast on sodium chloride prisms from 5–10% methylethyl ketone (MEK) solution. Attenuated total reflectance (ATR) measurements were carried out on thin strips of rubber placed on each side of the prism.

GEL-PERMEATION CHROMATOGRAPHY

Dilute solutions of the fluorosilicone gum in tetrahydrofuran (THF) were analyzed at ambient temperatures in a Model 200 gel-permeation chromatograph (Waters Associates, Inc.). Its four columns were packed with styrogel which had exclusion limits of 10^5, 10^4, 10^3, and 6 $\times$ 10^2 Å.

WEIGHT-LOSS MEASUREMENTS

Several samples of equal weight were heated at the desired temperatures. At certain intervals they were withdrawn and weighed. To minimize the temperature drop during sample withdrawal, the test oven was placed in a larger one at a slightly lower temperature. Thus, temperature drops could be held within 1 or 2°C.

STRESS-RELAXATION MEASUREMENTS

A specially constructed relaxometer, operable in either gas or liquid, to temperatures up to 315°C was used. This instrument (Figure 1) consists of a low-force-range load cell placed outside the oven; test specimen and the grips, housed in the gas-tight cylindrical test chamber mounted in the oven; and a movable cylinder attached to the lower grip which provides the desired elongation of the rubber specimen. The upper grip is attached to the load cell, which measures the force.

Specimens 25.4 by 69.8 mm were used at 28.5% extension. For intermittent stress-relaxation measurements, the rubber specimen was stretched for 10 min and relaxed for 60 min. For measurements in nitrogen, the chamber was first flushed several times with pure nitrogen, and thereafter a steady flow of the inert gas was maintained during the entire course of the test. For measurements in aircraft fuel (JP-4), the chamber was filled with the liquid from a reservoir connected to the chamber. The oven was flushed with nitrogen to minimize fire hazards.

The initial concentration of network-chains, ν_{e0}, was calculated by the equation

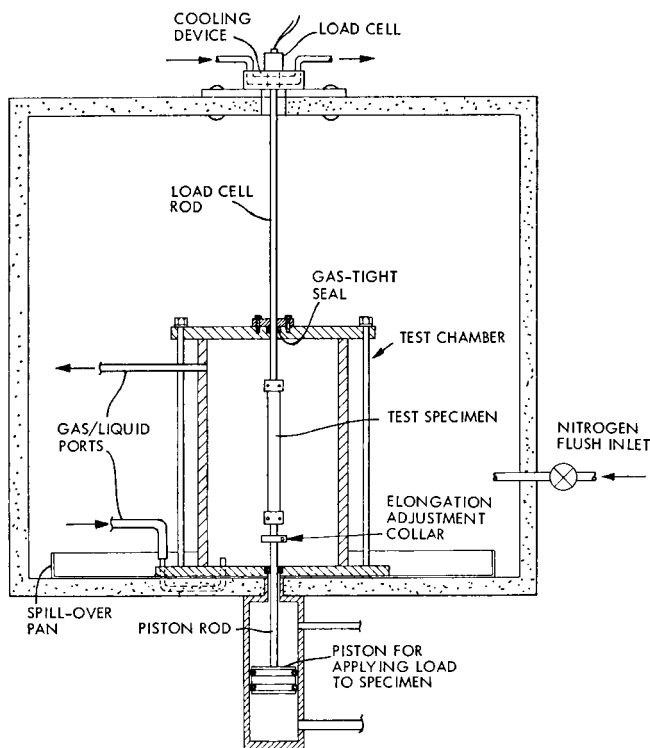$$\nu_{e0} = f_0/[ART(\lambda - \lambda^{-2})], \tag{1}$$

FIG. 1.—Schematic of high-temperature gas and liquid stress relaxometer.

where f_0 is the stress at time zero, A is the cross-sectional area of the unde-formed specimen, λ is the extension ratio, while R and T have their usual meaning.

RESULTS AND DISCUSSION

INFRARED STUDIES

No changes in the ir spectra were observed when samples of FVMQ gum were heated in air at 180–315°C, although, particularly at the higher tempera-tures, degradation was severe as evidenced by the high weight losses and the change in the physical condition of the samples. This indicates that although the polymer is breaking down into smaller fractions there is no alteration in the structure of the repeat unit of the elastomer or at least the change is less than 4–5%, the sensitivity limit for the ir instrument used. Elemental analyses of the degraded and undegraded polymer showed no significant change in composition indicating the absence of measurable concentration of new functional groups such as OH, OOH, or C=O. These results are unlike those obtained with the hydrocarbon rubber SBR[1], which on oxidation showed the presence of OH and C=O groups in the polymer network, the rates of their formation yielding useful kinetic data. Samples subjected to oxygen plasma at 20 P (0.15 mm Hg) showed no observable changes in the ir spectra although the samples showed hardening and crazing.

GEL-PERMEATION CHROMATOGRAPHY

The GPC chromatogram of the unheated FVMQ gum showed two peaks (Figure 2), the larger representing an average MW of 450 000 (polystyrene calibration) and the smaller a MW of 630 (polypropylene glycol calibration). Peak area measurements indicated 93–95% high-molecular-weight compound. A molecular weight of 624 corresponds to a tetramer of γ,γ',γ''-trifluoropropyl-methylsiloxane, the principal monomer of this FVMQ. Indications are that the tetramer is cyclic, because no end groups such as OH or OR were detected by ir or wet chemical analysis. Furthermore, the cyclic structure is a more stable configuration than the open chain.

As heat aging of the fluorosilicone progressed, GPC analysis showed a gradual increase in the concentration (increase in the peak area) of the 630 MW compound and a gradual decrease in that of the high-molecular-weight compound, suggesting the possibility of using GPC for degradation-rate studies. But this intent was complicated by the finding that THF, the solvent used in analysis, degrades the polymer even at room temperature. This was proved by the observed drop of viscosity and MW of THF solutions of the polymer with time. Moreover, the degradation was enhanced when the THF solution was filtered through an asbestos filter prior to GPC analysis. No acceleration was noticed when the solution was filtered through fritted glass. The pH of the asbestos was suspected as the cause of this phenomenon.

Other solvents that attacked FVMQ chemically in dilute solutions, were acetone and methylisobutyl ketone, both of which, like THF, are mildly nucleophilic and could attack the slightly positive silicone atom in the fluoro-propyl siloxane chain.

The GPC chromatograms also indicated that degradation or scission of the siloxane chain is random, as opposed to ordered unzipping of the repeating unit, because decrease in molecular weight was very rapid.
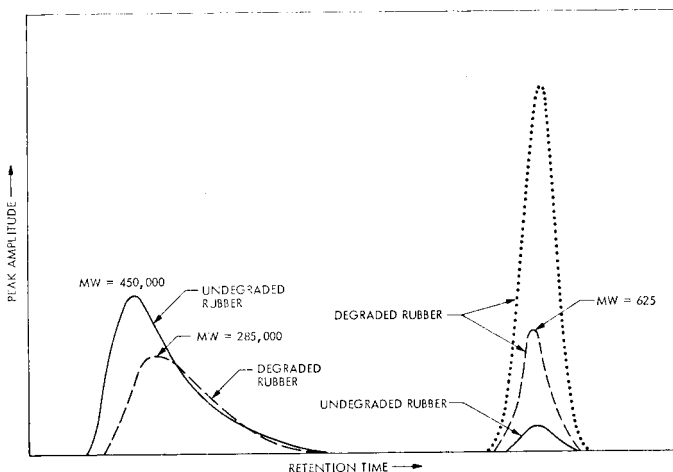

Fig. 2.—Gel-permeation chromatogram of FVMQ gum, 73h after preparation of solutions, and 1 h (———), 50h (– – – –), and 69h (. . .) after filtration through asbestos filter.
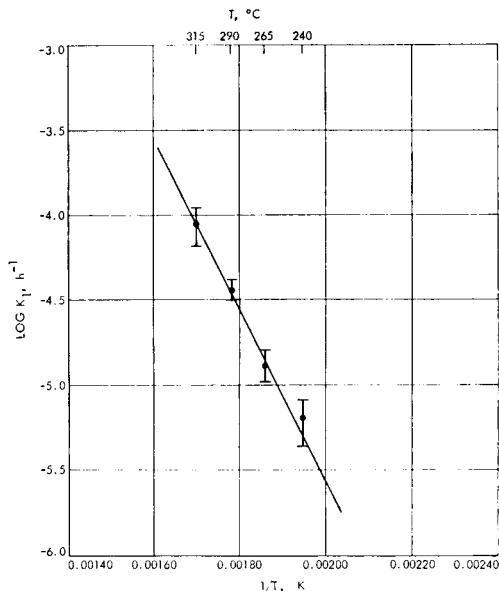
Fɪɢ. 3.—Temperature dependence of rate constants obtained from weight-loss measurements for fluorosilicone rubber.

WEIGHT-LOSS STUDIES

Studies of weight loss as a function of time were made in air at 240–315°C. The data obtained fitted a first-order rate equation. The Arrhenius plot yielded an activation energy, ΔE, of 103.7 kJ/mol (Figure 3).

STRESS-RELAXATION MEASUREMENTS

Stress relaxation is a valuable technique to obtain data of basic significance concerning the aging or the chemical degradation of elastomers[4]. The stress relaxation experiments were carried out with FVMQ in air, in nitrogen, and in JP-4 fuel. Some of the results of these experiments are shown in Figure 4, where the logarithms of the relative stress, f_t/f_0, are plotted as function of time. The symbols f_t and f_0 represent the tensile force at time t and t_0, respectively.

Data obtained from stress-relaxation measurements in air and nitrogen fitted a first-order rate equation up to 70% relaxation, whenever this extent of relaxation was attained. The first-order nature of the reaction was tested by the half-life and shift-factor methods. The activation energies obtained from the half-life and shift-factor methods with data obtained in the temperature range 150°–235°C were 152 kJ/mol and 158 kJ/mol, respectively (Figure 5). Half-life refers to the time it takes for the initial stress to decay 50%. The shift factors, $\log K_t$, were obtained by superposing (shifting along the logarithmic time axis) the f_t/f_0 vs. $\log t$ curves obtained at 235, 195, 180, and 150°C over that obtained at 215°C, the reference temperature. These activation energies are higher than those obtained from weight-loss measurements. This
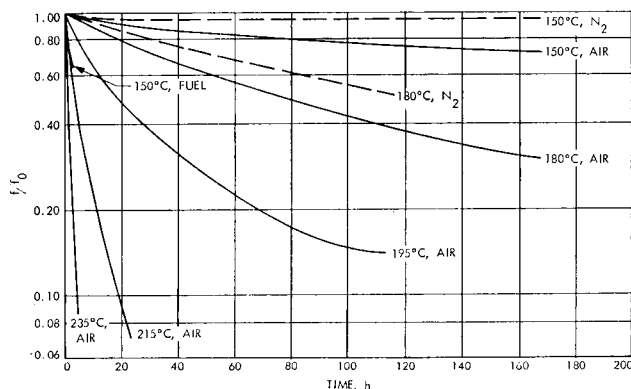
FIG. 4.—Effect of temperature on stress relaxation of peroxide-cured fluorosilicone rubber.

difference suggests that the two processes, chemical stress relaxation and thermal degradation are due to different reaction mechanisms, or that different reactions are occurring in the different temperature ranges, *i.e.*, 150–235°C for stress relaxation and 240–315°C for thermal measurements.
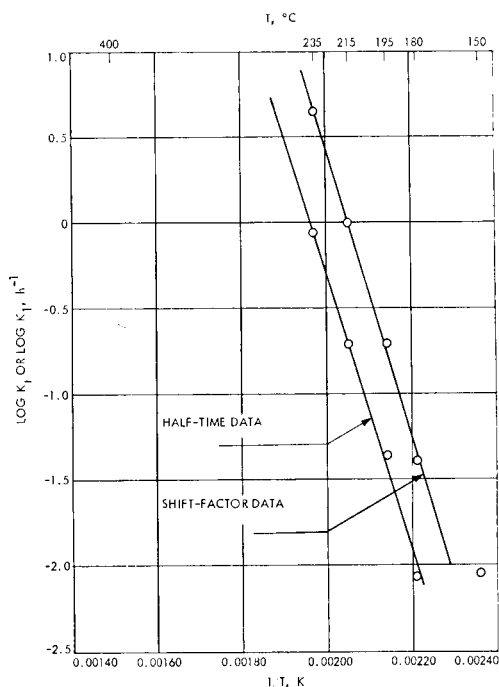

FIG. 5.—Temperature dependence of rate constants K_1 and K_t. $K_1 = 1/t_{\frac{1}{2}}$ and $K_t = 1/t$, where t is the time it takes to obtain the same amount of stress relaxation as at the reference temperature (215°C).
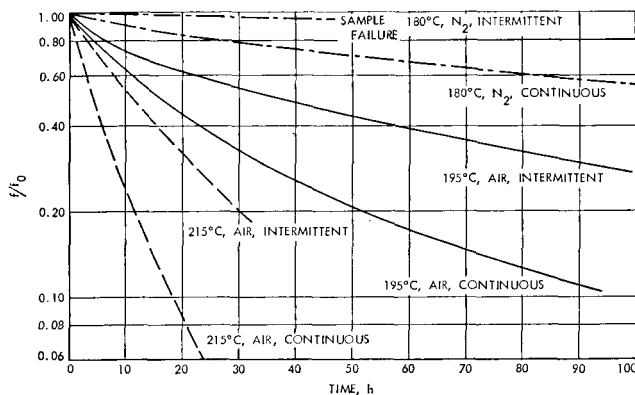
FIG. 6.—Continuous and intermittent stress relaxation of FVMQ at various temperatures in air and nitrogen.

Continuous and intermittent stress-relaxation measurements permit the determination of the number of new network chains, $\nu_e(t)$, formed during aging. Intermittent relaxation measures the net result of both scission and crosslinking during network breakdown. Continuous relaxation measures only the number of network chains which remain at any given time. Hence, at any given time the difference between the intermittent and continuous relaxation represents the contribution of newly formed network chains, i.e. the contribution of the crosslinking reaction[5]. The quantity $\nu_e(t)$ is given by

$$\nu_e(t) = \nu_e(0)[f^i(t) - f^c(t)]/f(0),   (2)$$

where $f(t)$ and $f(0)$ are the stresses at time t and t_0, respectively. The superscripts i and c denote intermittent and continuous stress relaxation respectively.

Examination of the intermittent and continuous stress-relaxation curves (Figure 6) shows that vulcanized FVMQ undergoes crosslinking during thermal aging in air at both 195°C and 215°C, the two temperatures at which intermittent runs were made. Figure 7 shows that crosslinking first increases and
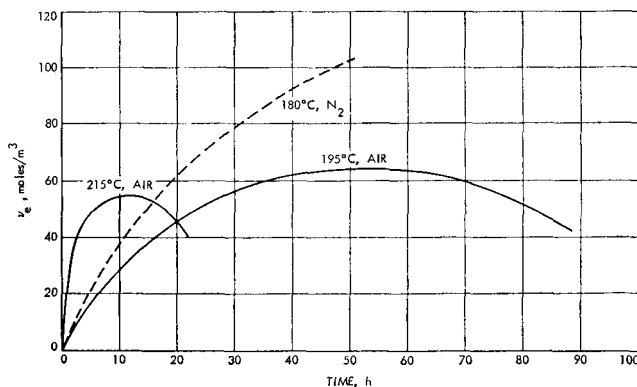

FIG. 7.—Additional network chains, ν_e, formed in FVMQ.

TABLE I

VALUES OF STRESS DECAY IN AIR AND NITROGEN

Test condition	Decay of tensile force, %	
	423 K	543 K
Air		
After 14 h	14	22
After 168 h	30	70
Nitrogen		
After 14 h	4	12
After 168 h	5	40

then decreases in air. The nitrogen experiment at 180°C (Figure 7) was discontinued after 50 h because of specimen failure. A leveling tendency, however, is observed in this case also.

Stress-relaxation curves obtained in pure nitrogen at 150°C and 180°C lie above those in air at the same temperatures (Figure 4), indicating that relaxation due to chemical changes is caused more by atmospheric oxygen than by thermal effects at the temperatures used. Values of stress decay in air and nitrogen are given in Table I.

It is of interest to know whether scission takes place randomly along the polymer chain, or at the crosslink sites. The crosslink in this FVMQ is probably formed from the vinyl free radical of one chain and the methyl group of another chain to give

$$
\begin{array}{ccc}
& | & | \\
& O & O \\
& | & | \\
CH_3-Si-CH_2-CH_2-CH_2-Si-R_F, \\
& | & | \\
& O & O \\
& | & |
\end{array}
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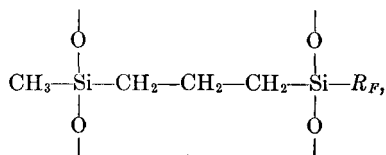
where R_F represents $-CH_2CH_2CF_3$.

It has been stated that random scission along the polymer chain is indicated when relaxation is found to be inversely proportional to the crosslink density, and scission at the crosslink is indicated when relaxation is independent of the crosslink density[4]. Stress relaxation of an FVMQ specimen cured with 0.05% dicumyl peroxide, which yields a rubber of lower crosslink density than the one more extensively used in this study, was much faster, suggesting that random scission along the polymer chain, rather than scission at the crosslink sites, predominates.

Random scission in the backbone chain involves the breaking of siloxane bonds, Si—O (bond energy, 369 kJ/mol[7]; other authors give even higher bond energies, ranging from 422 to 489 kJ/mol[3].) Scission at the crosslinks involves the breaking of Si—C or C—C bonds (bond energies, 290 and 348 kJ/mol[7], respectively). Although the siloxane bond is the strongest, its nearly 40% ionic character[3,9] makes it susceptible to nucleophilic and electrophilic attack. Thus, basic and acidic impurities, such as polymerization catalysts found in the rubber, will enhance the scission of the relatively stronger Si—O bond at higher temperatures. The random scission along the fluorosilicone polymer backbone is explainable on such grounds.

SUMMARY

The accelerated aging of a vulcanizate of fluorosilicone rubber was studied by four methods: infrared spectroscopy, GPC, weight loss, and stress relaxation, with the object of gathering information pertinent to understanding the basic mechanism of its aging. No changes were observed in infrared spectra of the rubber aged in air up to 315°C although severe degradation took place, as evidenced by high weight loss and drastic change in the physical condition of the test samples. It was concluded that although the polymer degrades, there is no change detectable within the precision of the analytical methods in the structure of the repeat unit of the elastomer. The gel-permeation chromatogram of unheated rubber showed peaks at MW 450 000 (95%) and 630 (5%). The low-molecular-weight component is very likely the cyclic tetramer of γ,γ',γ''-trifluoropropylmethylsiloxane, the principal monomer of the FVMQ used. Heat aging increased the concentration of the 630 MW component, but rate studies were prevented by complications resulting from solvent-induced rubber degradation. Rapid decrease in the MW of FVMQ, as found by GPC, indicated random scission in the polymer backbone, as opposed to ordered unzipping of the repeat unit. The same conclusion was reached from the effects of crosslink density on stress relaxation. Activation energies obtained from weight-loss measurements (104 kJ/mol) were lower than those obtained from stress-relaxation measurements, (150–155 kJ/mol), suggesting that the processes being measured in each case may not be the same. Chemical stress relaxation takes place more rapidly in the presence of air than in an inert atmosphere, and intermittent stress-relaxation measurements indicate that crosslinks form during thermal aging in air, their rate first increasing and then decreasing.

ACKNOWLEDGMENT

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